

# Vapour-liquid phase diagram for an ionic fluid in a random porous medium

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## Abstract

We study the vapour-liquid phase behaviour of an ionic fluid confined in a random porous matrix formed by uncharged hard sphere particles. The ionic fluid is modelled as an equimolar binary mixture of oppositely charged equisized hard spheres, the so-called restricted primitive model (RPM). Considering the matrix-fluid system as a partly-quenched model, we develop a theoretical approach which combines the method of collective variables with the extension of the scaled-particle theory (SPT) for a hard-sphere fluid confined in a disordered hard-sphere matrix. The approach allows us to formulate the perturbation theory using the SPT for the description of the thermodynamics of the reference system. The phase diagrams of the RPM in matrices of different porosities and for different size ratios of matrix and fluid particles are calculated in the random-phase approximation and also when the effects of higher-order correlations between ions are taken into account. Both approximations correctly reproduce the basic effects of porous media on the vapour-liquid phase diagram, i.e., with a decrease of porosity the critical point shifts toward lower fluid densities and lower temperatures and the coexistence region is getting narrower. For the fixed matrix porosity, both the critical temperature and the critical density increase with an increase of size of matrix particles and tend to the critical values of the bulk RPM.

## I. INTRODUCTION

This paper is devoted to the memory of George Stell who was one of the leaders in the statistical-mechanical theory of the liquid state for the last fifty years.

The study of the effects of an adsorbent on phase behaviour of an ionic fluid is far from being solved in spite of its great practical importance. To our knowledge, there is no theory capable of correctly describing the phase behaviour of confined ionic liquids even within the simplest models. By contrast, the phase transitions and criticality in bulk Coulomb-dominated systems have been intensively studied for the past decades. The issue was among the major research interests of George Stell [1]. For reviews of experimental and theoretical situation see [2–4] and the references cited therein. A simple description of systems dominated by Coulomb interactions is provided by the restricted primitive model (RPM) that consists of an equal number of equisized positively and negatively charged hard spheres immersed into structureless dielectric continuum. The RPM undergoes a vapour-liquid-like phase transition at low temperatures and low densities [1, 5–7].

The existing theoretical approaches consider fluids in disordered confinements as a partly-quenched system in which some of the degrees of freedom are quenched while the others are annealed [8]. In this case, statistical-mechanical averages used for calculations of thermodynamic properties become double ensemble averages: the first average is taken over all degrees of freedom of annealed particles keeping the quenched particles fixed, and the other average is performed over all realizations of a matrix. The application of the replica method made it possible to relate the matrix averaged quantities to the thermodynamic quantities of a corresponding fully equilibrated model, called the replicated model [9–12]. The major part of theoretical studies of partly-quenched systems containing charges was mainly focused on structural and thermodynamic properties within the framework of the replica Ornstein-Zernike (ROZ) theory (see review [13] and the references cited therein). The studies of the phase behaviour of partly-quenched models using the ROZ were concerned with the systems characterized by short-range interactions [14–16]. However, unlike bulk fluids, no analytical result has been obtained from the ROZ integral equation approach even for a hard-sphere fluid confined in a hard-sphere matrix, being the model of particular importance for the development of perturbation theories.

Recently, a pure analytical approach has been developed to describe the thermodynamics

of liquids confined in disordered porous materials composed of rigid particles [17–20]. This approach is based on the scaled-particle theory (SPT) [21] and is capable of rather correctly reproducing thermodynamic properties of confined fluids. Although the SPT is limited to hard-core interaction between molecules, it can be used for the description of a reference system within the perturbation theory to study different complex systems with attractive, repulsive, and associative interactions [22, 23].

The purpose of the present paper is to study the vapour-liquid phase behaviour of the RPM confined in a random porous matrix formed by uncharged particles. We start with a more general model when the interaction potentials between the two matrix particles and between the ion and the matrix particle include a short-range attraction/repulsion in addition to a hard-core repulsion. Furthermore, the ions and the matrix particles differ in size. Following the formalism originally proposed by Madden and Gland for a one-component system in a disordered porous matrix [8], we consider our matrix-fluid system as a partly-quenched model. Combining the collective variable (CV) method [24–27] with the SPT, we develop a theoretical approach which allows us to formulate the perturbation theory and to treat the model of an uncharged hard-sphere fluid in an uncharged hard-sphere matrix as a reference system. It should be noted that the CV method is a useful tool for the study of phase transitions in systems with Coulomb interactions [7, 28, 29]. Using the replica trick, we derive an expression for the grand partition function (GPF) of a wholly equilibrated  $(2s + 1)$ -component system in the form of a functional integral. In the limit  $s \rightarrow 0$ , we obtain explicit expressions for the Helmholtz free energy and the corresponding chemical potential of an ionic fluid in the random-phase approximation (RPA). For the particular case of neglecting matrix-matrix and matrix-fluid interactions outside the hard core, we calculate vapour-liquid coexistence curves of the RPM confined in hard-sphere matrices of different porosity. It should be noted that for the unconfined (bulk) state, the RPA, just as the standard Debye-Hückel theory and the mean-spherical approximation [1, 5], predicts the critical point parameters widely deviating from the simulation data [2]. In order to correct the situation we derive an explicit equation for the vapour-liquid spinodal using the method proposed in [7] for the bulk RPM. The method produces vapour-liquid critical parameters of the RPM in particular, the critical temperature, which are in good agreement with simulation results. The resulting equation for the spinodal includes isothermal compressibility of the reference system and its first and second derivatives. In this approximation, the trends of

the critical parameters (maximum points of the spinodals) with the matrix characteristics are the same as those obtained in the RPA.

The paper is arranged as follows. In section 2 we present a theoretical formalism. In section 3 we calculate the vapour-liquid phase diagrams of the RPM confined in a disordered hard-sphere matrix in two approximations, i.e., in the RPA and in the approximation which takes into account the effects of the higher-order correlations. The discussion of the effects of matrix properties on the phase diagrams is also presented here. We draw conclusions in section 4.

## II. THEORETICAL BACKGROUND

### A. Model

Our matrix/ionic-fluid system contains two subsystems: the first one (i.e., matrix) is composed of particles quenched or frozen in place, while the second subsystem is an annealed (or allowed to equilibrate) binary ionic fluid which is in equilibrium with the matrix. It is assumed that the matrix particles were quenched into an equilibrium configuration corresponding to the Gibbs distribution associated with a pairwise interaction potential  $u_{00}(x)$ . The ionic fluid is treated as the RPM. The interactions in the matrix/ionic-fluid system are described by a set of the pairwise interaction potentials:  $u_{00}(x)$ ,  $u_{++}(x) = u_{--}(x)$ ,  $u_{+-}(x) = u_{-+}(x)$ ,  $u_{0+}(x) = u_{+0}(x)$ ,  $u_{0-}(x) = u_{-0}(x)$ , where the subscript 0 refers to the matrix particles and the subscripts  $+$ ,  $-$  refer to the ions. We also assume that  $u_{0+}(x) = u_{0-}(x)$ .

The grand canonical potential of the system is given by [8]

$$-\beta\bar{\Omega}_1 = \frac{1}{\Xi_0} \sum_{N_0 \geq 0} \frac{z_0^{N_0}}{N_0!} \int d\mathbf{q}^{N_0} \exp[-\beta H_{00}(\mathbf{q}^{N_0})] \ln \Xi_1(\mathbf{q}^{N_0}),$$

where

$$\Xi_0 = \sum_{N_0 \geq 0} \frac{z_0^{N_0}}{N_0!} \int d\mathbf{q}^{N_0} \exp[-\beta H_{00}(\mathbf{q}^{N_0})]$$

is the GPF for the prequench medium,  $\mathbf{q}^{N_0} = \mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_{N_0}$  denotes the positions of the matrix particles,  $z_0$  is the activity of the matrix particles prior to quenching, and  $H_{00}(\mathbf{q}^{N_0})$  is the potential energy of the matrix particle configuration. The matrix-dependent GPF  $\Xi_1$

has the form:

$$\Xi_1(\mathbf{q}^{N_0}) = \sum_{N_+ \geq 0} \sum_{N_- \geq 0} \frac{z_+^{N_+} z_-^{N_-}}{N_+! N_-!} \int d\mathbf{r}^{N_+} d\mathbf{r}^{N_-} \exp\{-\beta[H_{0+}(\mathbf{r}^{N_+}, \mathbf{q}^{N_0}) + H_{0-}(\mathbf{r}^{N_-}, \mathbf{q}^{N_0}) + H_{++}(\mathbf{r}^{N_+}) + H_{--}(\mathbf{r}^{N_-}) + H_{+-}(\mathbf{r}^{N_+}, \mathbf{r}^{N_-})]\},$$

where  $z_A$  is the activity of the ions of species  $A$  ( $A = +, -$ ),  $\mathbf{r}^{N_A} = \mathbf{r}_1^A, \mathbf{r}_2^A, \dots, \mathbf{r}_{N_A}^A$  denotes the positions of the ions,  $H_{ij}$  describe the potential energy of the  $N_1 = N_+ + N_-$  ( $N_+ = N_-$ ) ions in the presence of matrix obstacles,  $\beta = 1/k_B T$  is the reciprocal temperature.

Following [11], we make use of the replica trick, which consists in replacing the logarithm with an exponential. As a result, we have

$$-\beta \bar{\Omega}_1 = \beta V \bar{P} = \lim_{s \rightarrow 0} \frac{d}{ds} \ln \Xi^{\text{rep}}(s), \quad (1)$$

where

$$\begin{aligned} \Xi^{\text{rep}}(s) &= \sum_{N_0 \geq 0} \sum_{N_1^+ \geq 0} \dots \sum_{N_s^+ \geq 0} \sum_{N_1^- \geq 0} \dots \sum_{N_s^- \geq 0} \frac{z_0^{N_0}}{N_0!} \prod_{\alpha=1}^s \frac{z_{+, \alpha}^{N_{\alpha}^+} z_{-, \alpha}^{N_{\alpha}^-}}{N_{\alpha}^+! N_{\alpha}^-!} \\ &\times \int d\mathbf{q}^{N_0} \prod_{\alpha=1}^s d\mathbf{r}_{\alpha}^{N_{\alpha}^+} d\mathbf{r}_{\alpha}^{N_{\alpha}^-} \exp\{-\beta H_{00} - \beta \sum_{\alpha=1}^s [H_{0+}^{\alpha} + H_{0-}^{\alpha}] \\ &- \beta \sum_{\alpha, \beta=1}^s [H_{++}^{\alpha\beta} + H_{+-}^{\alpha\beta} + H_{--}^{\alpha\beta}]\}. \end{aligned} \quad (2)$$

$\Xi^{\text{rep}}(s)$  is the GPF of a fully equilibrated  $(2s + 1)$ -component mixture, consisting of the matrix and of  $s$  identical copies or replicas of the two-component ionic fluid. Each pair of particles has the same pairwise interaction in this replicated system as in the partly quenched model except that a pair of ions from different replicas has no interaction

$$\begin{aligned} H_{00} &= \sum_{i < j}^{N_0} u_{00}(|\mathbf{q}_i - \mathbf{q}_j|), \quad H_{0A}^{\alpha} = \sum_{i < j}^{N_0, N_A^{\alpha}} u_{0A}^{\alpha}(\mathbf{r}_{\alpha, i}^A - \mathbf{q}_j|), \\ H_{AB}^{\alpha\beta} &= \sum_{i < j}^{N_{\alpha}^A, N_{\beta}^B} u_{AB}^{\alpha\beta}(|\mathbf{r}_{\alpha, i}^A - \mathbf{r}_{\beta, j}^B|) \delta_{\alpha\beta}. \end{aligned}$$

In the above equations, Greek indices  $\alpha, \beta$  denote replicas and Latin indices  $A, B$  denote ionic species,  $\mathbf{r}_{\alpha}^{N_A} = \mathbf{r}_{\alpha, 1}^A, \mathbf{r}_{\alpha, 2}^A, \dots, \mathbf{r}_{\alpha, N_A}^A$  is used for the set of charged particles of species  $A$  in replica  $\alpha$ . Since the replicated system is an equilibrium system, one can get the Helmholtz free energy using the Legendre transform

$$F^{\text{rep}}(s) = -\ln \Xi^{\text{rep}}(s) + \mu_0^{\text{rep}} N_0^{\text{rep}} + \sum_{\alpha=1}^{2s} \mu_{\alpha}^{\text{rep}} N_{\alpha}^{\text{rep}}. \quad (3)$$

Then, the free energy  $\overline{F}$  of the partly quenched system can be found from the equation

$$-\beta\overline{F} = \lim_{s \rightarrow 0} \frac{d}{ds}(-\beta F^{\text{rep}}). \quad (4)$$

## B. The method of collective variables

We assume that all the pairwise potentials between the different particles can be split into a reference part (index “r”) and a perturbation part (index “p”)

$$u_{ij}(x) = u_{ij}^{(r)}(x) + u_{ij}^{(p)}(x), \quad (5)$$

where  $u_{ij}^{(r)}(x)$  is a potential of a short-range repulsion which, generally, describes the mutual impenetrability of the particles, while  $u_{ij}^{(p)}(x)$  mainly describes the behaviour at moderate and large distances. The system in which the particles interact via the potentials  $u_{ij}^{(r)}(x)$  is regarded as the reference system,  $u_{ij}^{(r)}(x)$  is specified in the form of the hard-sphere potential. We assume that the thermodynamic and structural properties of the reference system are known. The interactions connected with potentials  $u_{ij}^{(p)}(x)$  are considered in the phase space of CVs.

Using the CV method we can get the exact functional representation of the GPF (2) [26, 27]

$$\begin{aligned} \Xi^{\text{rep}}(s) = & \int (d\rho_0)(d\omega_0)(d\rho_A^\alpha)(d\omega_A^\alpha) \exp \left[ -\frac{\beta}{2V} \sum_{\mathbf{k}} \tilde{u}_{00}^{(p)}(k) \rho_{\mathbf{k},0} \rho_{-\mathbf{k},0} \right. \\ & -\frac{\beta}{V} \sum_{\alpha} \sum_A \sum_{\mathbf{k}} \tilde{u}_{0A}^{\alpha(p)}(k) \rho_{\mathbf{k},0} \rho_{-\mathbf{k},A}^\alpha - \frac{\beta}{2V} \sum_{\alpha} \sum_{A,B} \sum_{\mathbf{k}} \tilde{u}_{AB}^{\alpha\alpha(p)}(k) \rho_{\mathbf{k},A}^\alpha \rho_{-\mathbf{k},B}^\alpha \\ & \left. + i \sum_{\mathbf{k}} \omega_{\mathbf{k},0} \rho_{\mathbf{k},0} + i \sum_{\alpha} \sum_A \sum_{\mathbf{k}} \omega_{\mathbf{k},A}^\alpha \rho_{\mathbf{k},A}^\alpha + \ln \Xi^r[\bar{\nu}_0 - i\omega_0, \bar{\nu}_A^\alpha - i\omega_A^\alpha] \right]. \quad (6) \end{aligned}$$

Here, the following notations are introduced:  $\rho_{\mathbf{k},0} = \rho_{\mathbf{k},0}^{(c)} - i\rho_{\mathbf{k},0}^{(s)}$  and  $\rho_{\mathbf{k},A}^\alpha = \rho_{\mathbf{k},A}^{\alpha(c)} - i\rho_{\mathbf{k},A}^{\alpha(s)}$  are the CVs which describe the fluctuation modes of the number of the matrix and fluid species, respectively, indices  $c$  and  $s$  denote real and imaginary parts of CVs,  $\omega_{\mathbf{k},0}$  and  $\omega_{\mathbf{k},A}^\alpha$  are conjugate to CVs  $\rho_{\mathbf{k},0}$  and  $\rho_{\mathbf{k},A}^\alpha$ , respectively.  $(d\rho_0)$  and  $(d\rho_A^\alpha)$  denote volume elements of the CV phase space

$$(d\rho_0) = d\rho_{0,0} \prod'_{\mathbf{k} \neq 0} d\rho_{\mathbf{k},0}^{(c)} d\rho_{\mathbf{k},0}^{(s)}, \quad (d\rho_A^\alpha) = \prod_{\alpha} \prod_{A=+,-} d\rho_{0,A}^\alpha \prod'_{\mathbf{k} \neq 0} d\rho_{\mathbf{k},A}^{\alpha(c)} d\rho_{\mathbf{k},A}^{\alpha(s)},$$

the product over  $\mathbf{k}$  is performed in the upper semi-space ( $\rho_{-\mathbf{k},0} = \rho_{\mathbf{k},0}^*$ ,  $\rho_{-\mathbf{k},A}^\alpha = \rho_{\mathbf{k},A}^{\alpha*}$ ). The same kind of relationships hold for  $(d\omega_0)$  and  $(d\omega_A^\alpha)$ . Coefficients  $\tilde{u}_{00}^{(p)}(k)$ ,  $\tilde{u}_{0A}^{\alpha(p)}(k)$  and  $\tilde{u}_{AB}^{\alpha\alpha(p)}(k)$  are the Fourier transforms of the corresponding interaction potentials.

$\Xi^r[\bar{\nu}_0 - i\omega_0, \bar{\nu}_A^\alpha - i\omega_A^\alpha]$  is the GPF of the reference system with the renormalized chemical potentials

$$\bar{\nu}_0 = \nu_0 + \frac{\beta}{2V} \sum_{\mathbf{k}} \tilde{u}_{00}^{(p)}(k), \quad \bar{\nu}_A^\alpha = \nu_A^\alpha + \frac{\beta}{2V} \sum_{\mathbf{k}} \tilde{u}_{AA}^{\alpha\alpha(p)}(k), \quad (7)$$

where  $\nu_0 = \beta\mu_0 - \ln \Lambda^3$  and  $\nu_A^\alpha = \beta\mu_A^\alpha - \ln \Lambda^3$  are the dimensionless chemical potentials of the corresponding species,  $\Lambda$  is the de Broglie thermal wavelength. In order to formulate the perturbation theory we apply a cumulant theorem to  $\ln \Xi^r$  [27]. As a result, equation (6) reads

$$\begin{aligned} \Xi^{\text{rep}}(s) = \Xi^{\text{mf}}[\tilde{\nu}_0, \tilde{\nu}_A^\alpha] \int (d\rho_0)(d\omega_0)(d\rho_A^\alpha)(d\omega_A^\alpha) \exp \left[ -\frac{\beta}{2} \sum_{\mathbf{k}} \hat{U}(k) \hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}} \right. \\ \left. + i \sum_{\mathbf{k}} \hat{\omega}_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} + \sum_{n \geq 2} \frac{(-i)^n}{n!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \hat{\mathfrak{M}}_n \hat{\omega}_{\mathbf{k}_1} \hat{\omega}_{\mathbf{k}_2} \dots \hat{\omega}_{\mathbf{k}_n} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n} \right]. \end{aligned} \quad (8)$$

where  $\Xi^{\text{mf}}$  is the mean-field part of the GPF

$$\Xi^{\text{mf}} = \Xi^r[\tilde{\nu}_0, \tilde{\nu}_A^\alpha] \exp \left\{ \langle N_0 \rangle_r \left[ \frac{\beta}{2} \bar{\rho}_0 \tilde{u}_{00}^{(p)}(0) + \sum_{\alpha} \sum_A \beta \bar{\rho}_A^\alpha \tilde{u}_{0A}^{\alpha(p)}(0) \right] \right\},$$

and  $\Xi^r$  depends on

$$\begin{aligned} \tilde{\nu}_0 &= \bar{\nu}_0 - \bar{\rho}_0 \beta \tilde{u}_{00}^{(p)}(0) - \sum_{\alpha} \sum_A \bar{\rho}_A^\alpha \beta \tilde{u}_{0A}^{\alpha(p)}(0), \\ \tilde{\nu}_A^\alpha &= \bar{\nu}_A^\alpha - \bar{\rho}_0 \beta \tilde{u}_{0A}^{\alpha(p)}(0) - \sum_B \bar{\rho}_B^\alpha \beta \tilde{u}_{AB}^{\alpha\alpha(p)}(0), \end{aligned} \quad (9)$$

$\bar{\rho}_0 = \langle N_0 \rangle_r / V$ ,  $\bar{\rho}_A^\alpha = \langle N_A^\alpha \rangle_r / V$ ,  $\langle \dots \rangle_r$  indicates the average taken over the reference system.

$\hat{U}(k)$  denotes a symmetric  $(2s+1) \times (2s+1)$  matrix of elements:

$$\begin{aligned} u_{11} &= \tilde{u}_{00}^{(p)}(k) = \tilde{\varphi}_{00}(k) \\ u_{1i} &= u_{i1} = \tilde{u}_{0A}^{\alpha(p)}(k) = \tilde{\varphi}_{0I}(k), \quad (i \geq 2), \\ u_{ii} &= \tilde{u}_{AA}^{\alpha\alpha(p)}(k) = \tilde{\varphi}^C(k), \quad (i \geq 2), \\ u_{ij} &= -\tilde{u}_{AA}^{\alpha\alpha(p)}(k) = -\tilde{\varphi}^C(k), \quad (2 \leq i \leq 2s, j = i+s), \\ u_{ij} &= 0, \quad (2 \leq i \leq 2s, j \neq i+s), \end{aligned} \quad (10)$$

$\tilde{\varphi}^C(k)$  is the Fourier transform of the Coulomb potential  $\varphi^C(r) = q^2/(\epsilon r)$ .  $\hat{\rho}_{\mathbf{k}}$  indicates a column vector of elements  $\rho_{\mathbf{k},0}, \rho_{\mathbf{k},+}^1, \dots, \rho_{\mathbf{k},+}^s, \rho_{\mathbf{k},-}^1, \dots, \rho_{\mathbf{k},-}^s$  and  $\hat{\omega}_{\mathbf{k}}$  is a row vector of elements  $\omega_{\mathbf{k},0}, \omega_{\mathbf{k},+}^1, \dots, \omega_{\mathbf{k},+}^s, \omega_{\mathbf{k},-}^1, \dots, \omega_{\mathbf{k},-}^s$ .  $\widehat{\mathfrak{M}}_n$  is a symmetric  $\underbrace{(2s+1) \times (2s+1) \times \dots \times (2s+1)}_n$  matrix whose elements are cumulants: the  $n$ th cumulant coincides with the Fourier transform of the  $n$ -particle connected correlation function of the reference system.

### C. Free energy of the ionic model in a disordered matrix: the random phase approximation

We consider the Gaussian approximation of the GPF putting  $n = 2$  in the cumulant expansion on the right-hand side of (8). In this case,  $\widehat{\mathfrak{M}}_2$  is a symmetric  $(2s+1) \times (2s+1)$  matrix. In the reference system, considered in this paper, the interaction potentials between the two fluid particles are equal (hard-sphere diameters of the ions are equal,  $\sigma_+ = \sigma_- = \sigma_1$ ) but, in general, they differ from those between the two matrix particles ( $\sigma_1 \neq \sigma_0$ ). In this case, the elements of matrix  $\widehat{\mathfrak{M}}_2$  are as follows:

$$\begin{aligned} m_{11} &= \mathfrak{M}_{00}(k), & m_{1i} = m_{i1} &= \mathfrak{M}_{01}(k), & (i \geq 2) \\ m_{ii} &= \mathfrak{M}_{11}(k), & (i \geq 2) \\ m_{ij} &= \mathfrak{M}_{12}(k), & (i, j \geq 2, i \neq j), \end{aligned}$$

where  $\mathfrak{M}_{ij}(k) = \langle N_i \rangle_r [\delta_{ij} + \bar{\rho}_j \tilde{h}_{ij}^r(k)]$ , the subscript 0 refers to the matrix particles and the subscripts 1 and 2 refer to the fluid,  $\tilde{h}_{ij}^r(k)$  is the Fourier transform of the total correlation function in the reference system. The determinant of matrix  $\widehat{\mathfrak{M}}_2$  has the form:

$$\det[\widehat{\mathfrak{M}}_2(s)] = (\mathfrak{M}_{11} - \mathfrak{M}_{12})^{2s-1} \Delta_1, \quad (11)$$

with  $\Delta_1 = 2s(\mathfrak{M}_{12}\mathfrak{M}_{00} - \mathfrak{M}_{01}^2) + \mathfrak{M}_{00}(\mathfrak{M}_{11} - \mathfrak{M}_{12})$ . For  $\sigma_+ = \sigma_-$ , we have  $\mathfrak{M}_{11} - \mathfrak{M}_{12} = \langle N_1 \rangle_r / 2$ .

After integration in (8), we arrive at the GPF of the replicated system in the Gaussian approximation

$$\begin{aligned} \frac{1}{V} \ln \Xi_G^{\text{rep}}(s) &= \frac{1}{V} \ln \Xi^r + \frac{\beta}{2} (\bar{\rho}_0)^2 \tilde{\varphi}_{00}(0) + s\beta \bar{\rho}_0 \bar{\rho}_1 \tilde{\varphi}_{0I}(0) \\ &\quad - \frac{1}{2V} \sum_{\mathbf{k}} \ln \left[ \det(\widehat{\mathfrak{M}}_2 \widehat{C}_2) \right], \end{aligned}$$



where  $\bar{\rho}_1 = \bar{\rho}_+ + \bar{\rho}_-$  and  $\hat{C}_2$  denotes a symmetric  $(2s+1) \times (2s+1)$  matrix of the Fourier transforms of the two-particle direct correlation functions in the Gaussian approximation. Its elements are as follows:

$$\begin{aligned}
c_{11} &= \tilde{C}_{00}(s) = \frac{\beta}{V} \tilde{\varphi}^{00}(k) + \frac{\mathfrak{M}_{11} + (2s-1)\mathfrak{M}_{12}}{\Delta_1}, \\
c_{1i} &= c_{i1} = \tilde{C}_{01}(s) = \frac{\beta}{V} \tilde{\varphi}^{0I}(k) - \frac{\mathfrak{M}_{01}}{\Delta_1}, \quad (i \geq 2), \\
c_{ii} &= \tilde{C}_{11}(s) = \frac{\beta}{V} \tilde{\varphi}^C(k) + \frac{\mathfrak{M}_{00}}{\Delta_1} + \frac{(2s-1)(\mathfrak{M}_{00}\mathfrak{M}_{12} - \mathfrak{M}_{01}^2)}{\Delta_2}, \quad (i \geq 2), \\
c_{ij} &= \tilde{C}_{12}(s) = -\frac{\beta}{V} \tilde{\varphi}^C(k) - \frac{\mathfrak{M}_{00}\mathfrak{M}_{12} - \mathfrak{M}_{01}^2}{\Delta_2}, \quad (2 \leq i \leq 2s, j = i+s), \\
c_{ij} &= \tilde{C}_{12}^{\alpha\beta}(s) = -\frac{\mathfrak{M}_{00}\mathfrak{M}_{12} - \mathfrak{M}_{01}^2}{\Delta_2}, \quad (2 \leq i \leq 2s, j \neq i+s),
\end{aligned} \tag{12}$$

where  $\Delta_2 = (\mathfrak{M}_{11} - \mathfrak{M}_{12})\Delta_1$ . Then, the determinant of matrix  $\hat{C}_2$  has the form:

$$\begin{aligned}
\det[\hat{C}_2(s)] &= \left( \tilde{C}_{11} - \tilde{C}_{12} \right)^s \left( \tilde{C}_{11} + \tilde{C}_{12} - 2\tilde{C}_{12}^{\alpha\beta} \right)^{s-1} \\
&\times \left\{ \tilde{C}_{00} \left[ \tilde{C}_{11} + \tilde{C}_{12} + 2(s-1)\tilde{C}_{12}^{\alpha\beta} \right] - 2s(\tilde{C}_{01})^2 \right\}.
\end{aligned} \tag{13}$$

Taking into account (11) and (12)-(13), we get the following expression for  $\ln \Xi_G^{\text{rep}}$

$$\begin{aligned}
\frac{1}{V} \ln \Xi_G^{\text{rep}}(s) &= \frac{1}{V} \ln \Xi^r + \frac{(\bar{\rho}_0)^2}{2} \beta \tilde{\varphi}^{00}(0) + s \bar{\rho}_0 \bar{\rho}_1 \beta \tilde{\varphi}^{0I}(0) \\
&- \frac{s}{2V} \sum_{\mathbf{k}} \ln [1 + \bar{\rho}_1 \beta \tilde{\varphi}^C(k)] - \frac{1}{2V} \sum_{\mathbf{k}} \ln [1 + \bar{\rho}_0 \beta \tilde{\varphi}^{00}(k) S_{00} \\
&+ 4s \sqrt{\bar{\rho}_0 \bar{\rho}_1} \beta \tilde{\varphi}^{0I}(k) S_{01} - 2s \bar{\rho}_0 \bar{\rho}_1 (\beta \tilde{\varphi}^{0I}(k))^2 \bar{\Delta}_1],
\end{aligned} \tag{14}$$

where  $S_{ij} = \mathfrak{M}_{ij} / \sqrt{\langle N_i \rangle_r \langle N_j \rangle_r}$  and  $\bar{\Delta}_1 = \Delta_1 / \langle N_0 \rangle_r \langle N_1 \rangle_r$ .

Using (3), (7) and (9) we arrive at the Helmholtz free energy per volume of the replicated system,  $\beta f = \beta F^{\text{rep}}/V$ , in the RPA

$$\begin{aligned}
\beta f_{\text{RPA}} &= \beta f^r(s) - \frac{\rho_0^{\text{rep}}}{2V} \sum_{\mathbf{k}} \beta \tilde{\varphi}^{00}(k) - s \frac{\rho_1^{\text{rep}}}{2V} \sum_{\mathbf{k}} \beta \tilde{\varphi}^C(k) \\
&+ \frac{(\rho_0^{\text{rep}})^2}{2} \beta \tilde{\varphi}^{00}(0) + s \rho_0^{\text{rep}} \rho_1^{\text{rep}} \beta \tilde{\varphi}^{0I}(0) + \frac{s}{2V} \sum_{\mathbf{k}} \ln [1 + \rho_1^{\text{rep}} \beta \tilde{\varphi}^C(k)] \\
&+ \frac{1}{2V} \sum_{\mathbf{k}} \ln \left[ 1 + \rho_0^{\text{rep}} \beta \tilde{\varphi}^{00}(k) S_{00} + 4s \sqrt{\rho_0^{\text{rep}} \rho_1^{\text{rep}}} \beta \tilde{\varphi}^{0I}(k) S_{01} \right. \\
&\left. - 2s \rho_0^{\text{rep}} \rho_1^{\text{rep}} (\beta \tilde{\varphi}^{0I}(k))^2 \bar{\Delta}_1 \right],
\end{aligned}$$

where  $f^r$  is the free energy of the reference system.  $\rho_0^{\text{rep}}$  and  $\rho_1^{\text{rep}}$  denote the number densities of the matrix and fluid particles, respectively.

Finally, taking a replica limit (4), we find the following expression for the RPA free energy of a model ionic fluid in a disordered matrix

$$\begin{aligned}
\beta \bar{f}_{\text{RPA}} = & \beta \bar{f}^r - \frac{1}{2V} \sum_{\mathbf{k}} \beta \tilde{\varphi}^{00}(k) \left. \frac{d}{ds} \right|_{s=0} \rho_0^{\text{rep}} - \frac{\rho_1}{2V} \sum_{\mathbf{k}} \beta \tilde{\varphi}^C(k) \\
& + \beta \tilde{\varphi}^{00}(0) \rho_0 \left. \frac{d}{ds} \right|_{s=0} \rho_0^{\text{rep}} + \rho_0 \rho_1 \beta \tilde{\varphi}^{0I}(0) + \frac{1}{2V} \sum_{\mathbf{k}} \ln [1 + \rho_1 \beta \tilde{\varphi}^C(k)] \\
& + \frac{1}{2V} \sum_{\mathbf{k}} \left\{ \left[ \beta \tilde{\varphi}^{00}(k) \left. \frac{d}{ds} \right|_{s=0} (\rho_0^{\text{rep}} S_{00}) + 4 \beta \tilde{\varphi}^{0I}(k) \sqrt{\rho_0 \rho_1} S_{01} \right]_{s=0} \right. \\
& \left. - (\beta \tilde{\varphi}^{0I}(k))^2 \rho_0 \rho_1 S_{00} \right|_{s=0} \Big/ [1 + \beta \tilde{\varphi}^{00}(k) \rho_0 S_{00} \Big|_{s=0}] \Big\}. \tag{15}
\end{aligned}$$

In the above equation, the notations  $\rho_0 = \rho_0^{\text{rep}}|_{s=0}$  and  $\rho_1 = \rho_1^{\text{rep}}|_{s=0}$  are introduced.

Hereafter, we put  $\tilde{\varphi}^{00}(k) = 0$  and  $\tilde{\varphi}^{0I}(k) = 0$  which corresponds to neglecting the perturbative parts of the interaction potentials between the matrix particles and between the matrix particles and the ions (see (5) and (10)). As a result, (15) reduces to the form:

$$\beta \bar{f}_{\text{RPA}} - \beta \bar{f}^r = -\frac{\rho_1}{2V} \sum_{\mathbf{k}} \beta \tilde{\varphi}^C(k) + \frac{1}{2V} \sum_{\mathbf{k}} \ln [1 + \rho_1 \beta \tilde{\varphi}^C(k)].$$

The term on the right-hand side of the above equation arises from the electrostatic interactions between the ions. It is of the same form as the corresponding contribution to the free energy of the RPM in the bulk [28]. The main difference between the bulk RPM and the RPM confined in a hard-sphere matrix is given by the term  $\bar{f}^r$  describing the contribution from the reference system. Accordingly, the perturbative part of the chemical potential ( $\mu_1 = \mu_+ = \mu_-$ ) of the ions in the presence of a hard-sphere matrix reads

$$\bar{\mu}_1^{\text{RPA}} - \bar{\mu}_1^r = -\frac{1}{2V} \sum_{\mathbf{k}} \tilde{\varphi}^C(k) - \frac{\beta^{-1}}{2V} \sum_{\mathbf{k}} \tilde{g}(k), \tag{16}$$

where

$$\tilde{g}(k) = -\frac{\beta \tilde{\varphi}^C(k)}{1 + \rho_1 \beta \tilde{\varphi}^C(k)} \tag{17}$$

and  $\bar{\mu}_1^r$  is a part of the chemical potential connected with in the reference system.

#### D. Beyond the random-phase approximation

Although the RPA gives a good qualitative description of the vapour-liquid phase behaviour of the RPM fluid, it is still essentially far from a quantitative agreement with the

computer simulation results [2]. This general disadvantage of the RPA can be corrected by taking into account the effects of higher-order fluctuations.

In order to go beyond the RPA we use the method proposed for an ionic model in the bulk [7, 28]. We start with the expression for  $\beta\overline{P}_G$

$$\beta\overline{P}_G = \beta\overline{P}^r - \frac{1}{2V} \sum_{\mathbf{k}} \ln [1 + \rho_1 \beta \tilde{\varphi}^C(k)],$$

obtained with the use of (1) and (14) under conditions  $\tilde{\varphi}^{00}(k) = 0$  and  $\tilde{\varphi}^{0I}(k) = 0$ . Here,  $\overline{P}^r = (dP^r/ds)|_{s=0}$ , and  $\rho_1 = \bar{\rho}_1|_{s=0}$ . Both  $\overline{P}^r$  and  $\rho_1$  depend on the chemical potential  $\bar{\mu}_1$ . Presenting the chemical potential as  $\beta\bar{\mu}_1 = \beta\bar{\mu}_1^r + \Delta\nu_1$ , we expand  $\beta\overline{P}_G$  in powers of  $\Delta\nu_1$  up to the fourth power

$$\beta\overline{P}_G = \sum_{n=0}^4 \frac{\mathcal{M}_n}{n!} \Delta\nu_1^n,$$

where  $\mathcal{M}_n = \partial^n(\beta\overline{P}_G)/\partial\Delta\nu_1^n|_{\Delta\nu_1=0}$ . Following the procedure described in [7, 28] for the bulk RPM, we get the equation for the vapour-liquid spinodal of the RPM confined in a random hard-sphere matrix

$$\frac{1}{V} \sum_{\mathbf{k}} \tilde{g}(k) = -2 \frac{\overline{\mathfrak{M}}_2}{\overline{\mathfrak{M}}_3} + \frac{\overline{\mathfrak{M}}_3}{\overline{\mathfrak{M}}_4}, \quad (18)$$

where  $\tilde{g}(k)$  is given in (17) and

$$S_n = \frac{\overline{\mathfrak{M}}_n}{\rho_1} = \frac{\partial^n \beta\overline{P}^r}{\partial(\beta\bar{\mu}_1^r)^n}, \quad n \geq 2 \quad (19)$$

are determined from the thermodynamics of the reference system. In particular,  $S_2$  is connected with the isothermal compressibility of the reference system

$$S_2 = \rho_1 k_B T \kappa_T = \left[ \left( \frac{\partial \beta\overline{P}^r}{\partial \rho_1} \right)_T \right]^{-1}. \quad (20)$$

Explicit expressions for  $S_2$ ,  $S_3$  and  $S_4$  are given in Appendix.

### E. Thermodynamics of the reference system: The scaled-particle theory

In order to describe the thermodynamic properties of the reference system needed in this perturbation scheme we use the SPT theory reformulated recently for a hard-sphere fluid in a quenched hard-sphere matrix forming a random porous medium. Here, we only outline the main ideas of the theory and present the expressions for the chemical potential and pressure

of a hard-sphere fluid in a disordered matrix which will be used in the current study. One can find a detailed presentation of the SPT theory in [17, 18].

The basic idea of the SPT approach is an insertion of an additional scaled particle of a variable size into a fluid. The procedure of the insertion is equivalent to the creation of a cavity which is free of any other fluid particles. The key point of the considered reformulation of the SPT theory consists in a derivation of the excess chemical potential of a scaled particle  $\mu_s^{ex}$ , which is equal to work needed to introduce the particle of radius  $r_s$  into a fluid in the presence of matrix particles.

An exact expression for a point scaled particle in a hard-sphere fluid in a random porous medium was obtained in [30]. Combining this expression with the thermodynamic consideration of the large scaled particle, the chemical potential for a hard-sphere fluid in a hard-sphere matrix was obtained. However, the approach proposed in [30] referred to as SPT1 contains a subtle inconsistency appearing when the size of matrix particles is essentially larger than the size of fluid particles. Later, this inconsistency was eliminated in a new approach named as SPT2 [31]. Starting from this formalism a series of new approximations were developed [17, 18, 31]. Among these approximations we distinguish the SPT2b1 approximation which was approved as the most accurate one being in a very good agreement with the Monte-Carlo simulation results [22]. The expressions obtained in SPT2b1 are used in our paper for the description of the reference system. Consequently, we can write the following expression for the chemical potential  $\bar{\mu}_1^r$

$$(\beta\bar{\mu}_1^r)^{SPT2b1} = \ln(\Lambda_1^3\rho_1) - \ln(\phi) - \ln(1 - \eta_1/\phi_0) + (1 + A)\frac{\eta_1/\phi_0}{1 - \eta_1/\phi_0} + \frac{\eta_1(\phi_0 - \phi)}{\phi_0\phi(1 - \eta_1/\phi_0)} + \frac{1}{2}(A + 2B)\frac{(\eta_1/\phi_0)^2}{(1 - \eta_1/\phi_0)^2} + \frac{2}{3}B\frac{(\eta_1/\phi_0)^3}{(1 - \eta_1/\phi_0)^3}. \quad (21)$$

Here, the following notations are introduced.  $\eta_0 = \frac{\pi}{6}\rho_0\sigma_0^3$  and  $\eta_1 = \frac{\pi}{6}\rho_1\sigma_1^3$  are the packing fractions of the matrix and fluid particles, respectively.  $\phi_0$  is the geometrical porosity:  $\phi_0 = 1 - \eta_0$ . The second type of porosity  $\phi$ , called the probe-particle porosity, is defined by the excess chemical potential of a fluid in the limit of infinite dilution [31]. It has the form:

$$\phi = (1 - \eta_0) \exp \left[ - \left( \frac{3\eta_0\tau}{1 - \eta_0} + \frac{3\eta_0(1 + \frac{1}{2}\eta_0)\tau^2}{(1 - \eta_0)^2} + \frac{\beta P_0\eta_0\tau^3}{\rho_0} \right) \right], \quad (22)$$

where  $\tau = \sigma_1/\sigma_0$ , and

$$\frac{\beta P_0}{\rho_0} = \frac{(1 + \eta_0 + \eta_0^2)}{(1 - \eta_0)^3}.$$

Coefficients  $A$  and  $B$ , which determine the porous medium structure, are as follows:

$$A = 6 + \frac{3\eta_0\tau(\tau+4)}{1-\eta_0} + \frac{9\eta_0^2\tau^2}{(1-\eta_0)^2}$$

$$B = \frac{9}{2} \left(1 + \frac{\tau\eta_0}{1-\eta_0}\right)^2$$

The expression for the pressure obtained by using (21) and the Gibbs-Duhem equation reads

$$\left(\frac{\beta\bar{P}^r}{\rho_1}\right)^{SPT2b1} = -\frac{\phi_0}{\phi} \frac{1}{(1-\eta_1/\phi_0)} + \frac{\phi_0}{\eta_1} \left(\frac{\phi_0}{\phi} - 1\right) \ln\left(1 - \frac{\eta_1}{\phi_0}\right)$$

$$+ \frac{A}{2} \frac{\eta_1/\phi_0}{(1-\eta_1/\phi_0)^2} + \frac{2B}{3} \frac{(\eta_1/\phi_0)^2}{(1-\eta_1/\phi_0)^3}. \quad (23)$$

### III. RESULTS AND DISCUSSIONS

Using the theory described above we study the vapour-liquid phase diagram of the RPM confined in a hard-sphere matrix depending on the matrix properties (porosities  $\phi_0$  and  $\phi$ ) as well as on the parameter of size asymmetry  $\tau$ . The calculations are performed in two approximations: the RPA and the approximation when the correlation effects of higher than the second order are taken into account (equation (18)). We use the Weeks-Chandler-Andersen regularization scheme [32] for the Coulomb potential inside the hard core. In this case,  $\tilde{\varphi}^C(k) = 4\pi q^2 \sin(k\sigma_1)/(\epsilon k^3)$ . Hereafter, the following reduced units are introduced for the temperature  $T^* = k_B T \epsilon \sigma_1 / q^2$  and for the density  $\rho^* = \rho \sigma_1^3$ .

#### A. Vapour-liquid binodals obtained in the RPA

In order to calculate the coexistence curves we use equations (16)-(17) and (21) for the chemical potential and employ the Maxwell double-tangent construction. First, we consider the binodals of vapour-liquid diagrams for the RPM fluid in the matrices of different probe-particle porosities,  $\phi$ , but at the fixed size ratio of the fluid and matrix particles,  $\tau = 1$  (figure 1). As one can observe, both the critical temperature  $T_c^*$  and the critical densities  $\rho_c^*$  are lowering with the decrease of the matrix porosity. Simultaneously, the region of vapour-liquid coexistence is getting narrower. This common behaviour is observed for many other types of fluids. Since our model does not contain any attractive interactions between the fluid and matrix particles, only two most essential effects can play the role: the effect of

excluded volume occupied by the matrix particles and the weakening of attraction between the fluid particles due to the presence of matrix particles. In comparison with the bulk fluid ( $\phi = 1.0$ ), the first effect leads to an increase of the fluid local density that is why the total density can be smaller than in the bulk case. The second effect lowers an average coordination number of fluid particles due to a contact of the fluid with a pore surface formed by the matrix particles, hence the effective attraction in such a system is less than in the bulk. Thus, the critical temperature can decrease. This is typical of most liquids and our results show that ionic liquids are not an exception, at least for the RPM within the RPA.

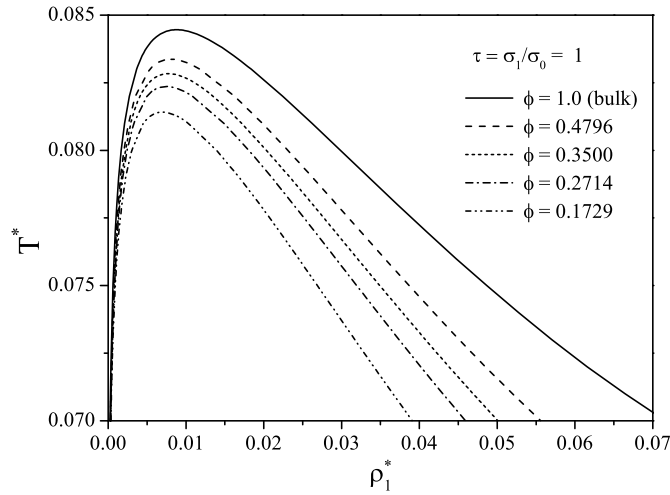


FIG. 1: Vapour-liquid coexistence curves for the RPM fluid confined in a hard-sphere matrix at different porosities, but at the fixed size ratio  $\tau = 1$ . The results are obtained in the RPA.

As it was mentioned above, we distinguish two types of porosity: the probe-particle porosity  $\phi$  and the geometrical porosity  $\phi_0$ . A principal difference between them consists in the fact that the porosity  $\phi$  takes into account the size of adsorbate particles, while the porosity  $\phi_0$  is an adsorbate-independent characteristic. Both of these porosities are important. The geometrical porosity defines a "bare" pore volume of the matrix and it can be considered as a more general characteristic. On the other hand, it does not take into account that some pores are inaccessible for the given fluid molecules due to their sizes: a distance between the opposite pore walls can be less than the diameter of fluid particles. By contrast, the probe-particle porosity  $\phi$  defines a "real" pore volume, which is accessible for the fluid under study.

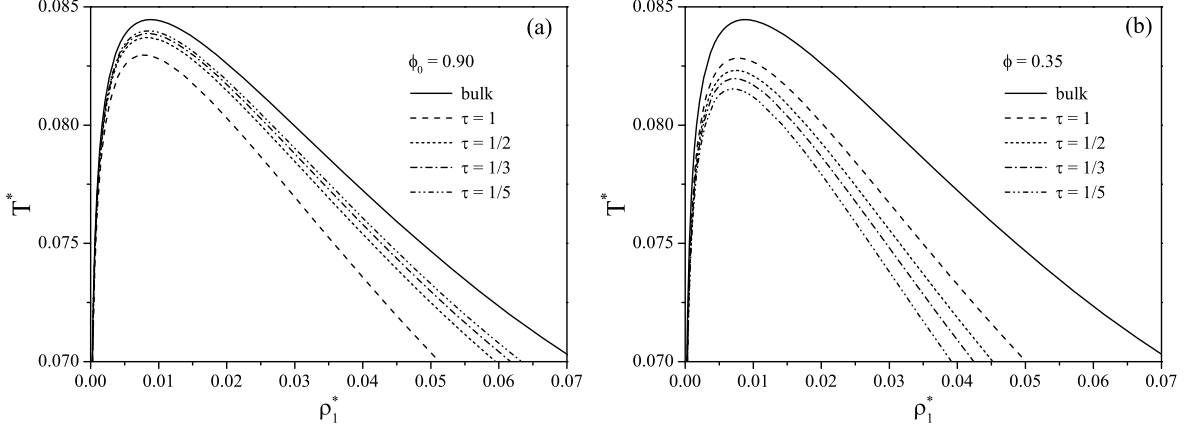


FIG. 2: Vapour-liquid coexistence curves for the RPM fluid confined in a hard-sphere matrix at different size ratios  $\tau$ , but at the fixed porosities  $\phi_0 = 0.90$  (a) and  $\phi = 0.35$  (b). The results are obtained in the RPA.

Regardless of which type of the porosities is under control, a decrease both of them leads to a decrease of the critical parameters  $T_c^*$  and  $\rho_c^*$ . However, the effect of the size ratio parameter  $\tau$  is more ambiguous. In figure 2 we present vapour-liquid phase diagrams for the RPM fluid in matrices formed by particles of different sizes, but at constant porosities  $\phi_0$  (panel a) and  $\phi$  (panel b). As one can see, there are opposite dependencies of critical parameters on the ratio of fluid and matrix particles  $\tau$ . To understand this behaviour it should be noted that the probe-particle porosity is always less than or equal to the geometrical porosity ( $\phi \leq \phi_0$ ). Moreover, both porosities become equivalent in the limit  $\tau \rightarrow 0$ , when a bulk-like fluid at the effective density  $\eta_1^* = \eta_1/\phi$  is obtained [31]. The bulk-like fluid can be reached due to a negligibly small effect of a pore surface in this limit: a specific pore surface area vanishes with respect to the specific free volume. Hence, the fraction of inaccessible pores in the system tends to zero as well. Therefore, if the porosity  $\phi_0$  is fixed and the ratio  $\tau$  decreases (figure 2a), then the porosity  $\phi$  increases. As it is shown in the previous figure, an increase of the porosity  $\phi$  leads to an increase of  $T_c^*$  and  $\rho_c^*$ . In the case when the porosity  $\phi$  is constant, but  $\tau$  decreases (figure 2b), one observes that the critical temperature and density decrease as well. This seeming contradiction can be explained by the fact that the specific free volume which makes a greater contribution to the thermodynamics of the system than the specific pore surface area effect, decreases in this case.

Based on the results presented in figure 2a we demonstrate quantitative estimations of

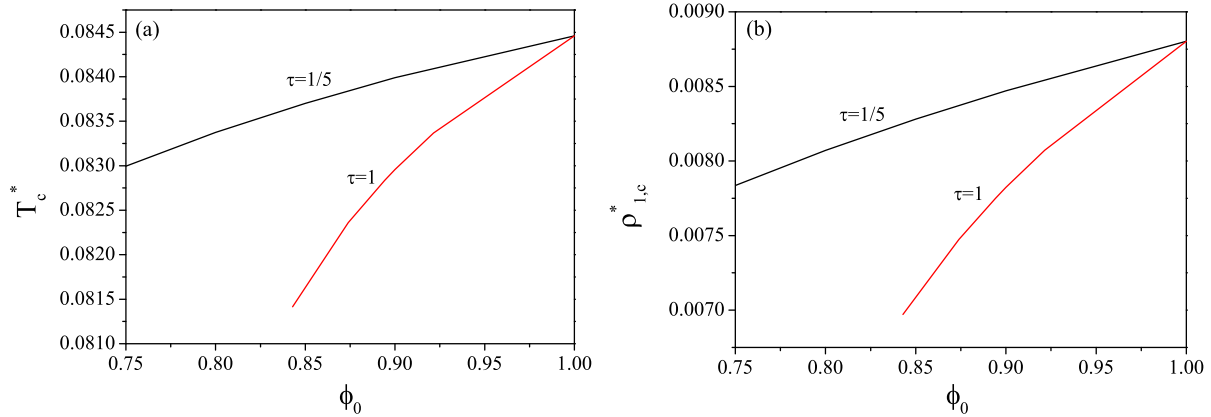


FIG. 3: Critical temperature  $T_c^*$  (a) and critical density  $\rho_{1,c}^*$  (b) of the RPM fluid confined in a hard-sphere matrix depending on the matrix porosity  $\phi_0$ . The results are obtained in the RPA.

the critical parameters  $T_c^*$  and  $\rho_c^*$  depending on the porosity  $\phi_0$  for the small and larger matrix particles (figure 3). It is clearly seen that the both critical parameters increase monotonously with increasing  $\phi_0$ . Naturally, for large matrix particles ( $\tau = 1/5$ )  $T_c^*$  and  $\rho_c^*$  are higher than in the case of small matrix particles ( $\tau = 1$ ) everywhere until the bulk case is obtained ( $\phi_0 = 1$ ), where they become equal.

### B. Vapour-liquid spinodals obtained with taking into account higher-order terms

In our previous studies of a vapour-liquid phase transition of the RPM fluid in the bulk [7] we demonstrated that the higher-order terms being taken into account essentially improved the results and led to the value of the critical temperature  $T_c^* = 0.0502$ , which is rather close to the one obtained from the computer simulations ( $T_c^* = 0.049$ ) [2]. In comparison, the RPA strongly overestimates the critical temperature by giving  $T_c^* = 0.084$  [6, 7]. The critical density obtained in the above-mentioned approximation is still underestimated ( $\rho_c^* = 0.044$ ) when compared with the simulation results ( $\rho_c^* = 0.06 - 0.08$ ) [2], but it is much better than in the case of the RPA giving  $\rho_c^* \simeq 0.01$  [6, 7]. Such an improvement achieved when the effects of higher-order correlations are taken into account has motivated us to extend this approach to the case of the RPM fluid confined in a hard-sphere matrix.

Using (18) and (17) in a combination with equations (A24)-(A29) we have calculated spinodals for the vapour-liquid phase transition of the RPM fluid in matrices of different



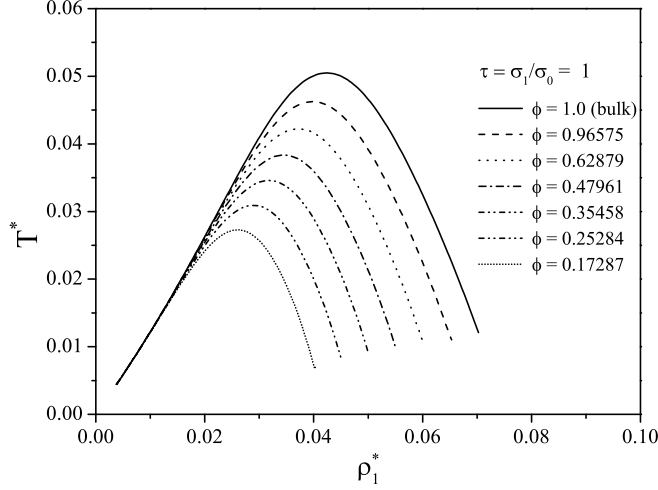


FIG. 4: Vapour-liquid spinodal curves for the RPM fluid confined in a hard-sphere matrix at different porosities, but at the fixed size ratio  $\tau = 1$ . The results are obtained by using equation (18).

porosities  $\phi$ , but at the constant value of  $\tau = 1$  (figure 4). From the obtained results one can observe the same qualitative dependence of the critical temperature and density on the matrix porosity, i.e. both parameters decrease with a decrease of  $\phi$ . However, it is seen that in comparison with the RPA results (figure 1) the critical parameters obtained in the approximation given by (18) are more sensible to the variation of matrix porosity.

The effect of the matrix particle size at fixed porosities  $\phi_0 = 0.90$  and  $\phi = 0.35$  is shown in figure 5. For these cases, one can notice the same tendencies as the ones obtained in the RPA, but again both critical parameters are lowering faster with a decrease of  $\tau$ . Therefore, it should be acknowledged that this sensibility to the matrix porosity is directly related to taking into account the higher-order terms.

The quantitative analysis of the critical temperature and density behaviour shows not only their rapid and monotonous variation with respect to the matrix porosity  $\phi_0$  (figure 6) in comparison with the RPA results (figure 3), but also these dependencies are very close to linear ones. This is one more distinction between the RPA and the results obtained in the higher-order approximation. As usual,  $T_c^*$  and  $\rho_c^*$  for smaller matrix particles ( $\tau = 1$ ) are lower than for larger ones ( $\tau = 1/5$ ). Besides that, we have estimated the limit case  $\tau \rightarrow 0$  (infinite size of matrix particles) shown by dashed lines in figure 6 which is the upper bound

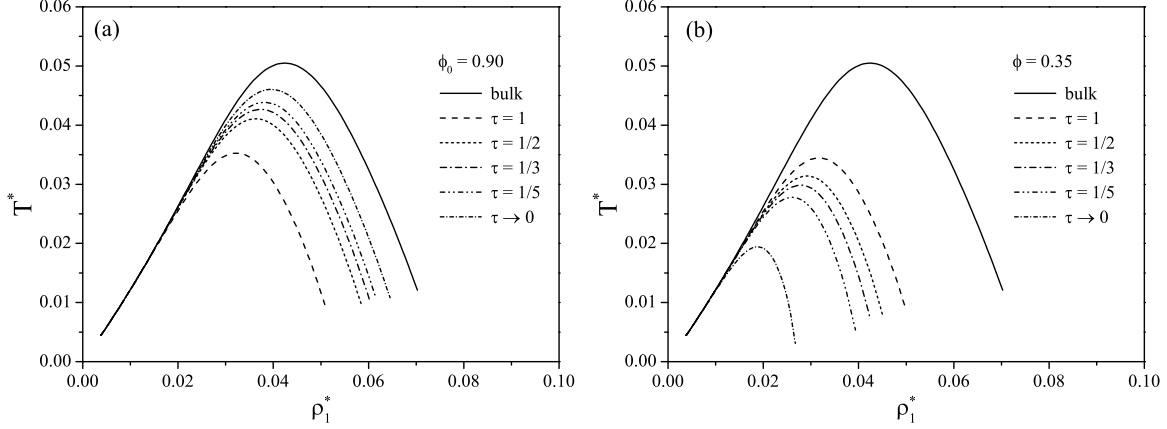


FIG. 5: Vapour-liquid spinodal curves for the RPM fluid confined in a hard-sphere matrix at different size ratios  $\tau$ , but at the fixed porosities  $\phi_0 = 0.90$  (a) and  $\phi = 0.35$  (b). The results are obtained by using equation (18).

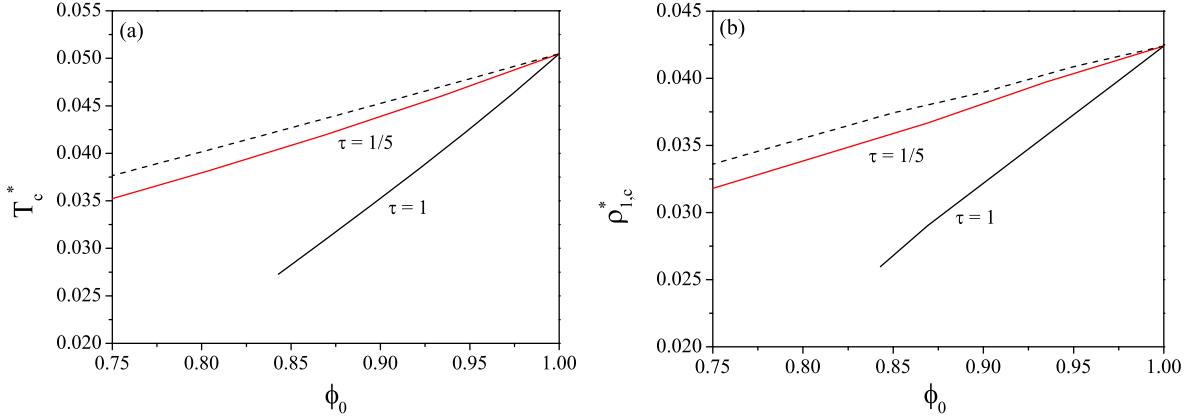


FIG. 6: Critical temperature  $T_c^*$  (a) and critical density  $\rho_{1,c}^*$  (b) of the RPM fluid confined in a hard-sphere matrix depending on the matrix porosity  $\phi_0$ . Dashed line corresponds to the limit  $\tau \rightarrow 0$  (or  $\sigma_0/\sigma_1 \rightarrow \infty$ ). The results are obtained by using equation (18).

of the corresponding critical parameters at the given matrix porosities.

Finally, we have built plots for the critical parameters in the  $T_c^*$ - $\rho_c^*$  coordinates for the porosities  $\phi_0 = 0.90$  (figure 7a) and  $\phi = 0.35$  (figure 7b) and for different values of ratio parameter  $\tau$ . One can notice interesting dependencies for the both cases, where a linear behaviour is obtained. The same type of behaviour is found for the critical parameters obtained in the RPA.

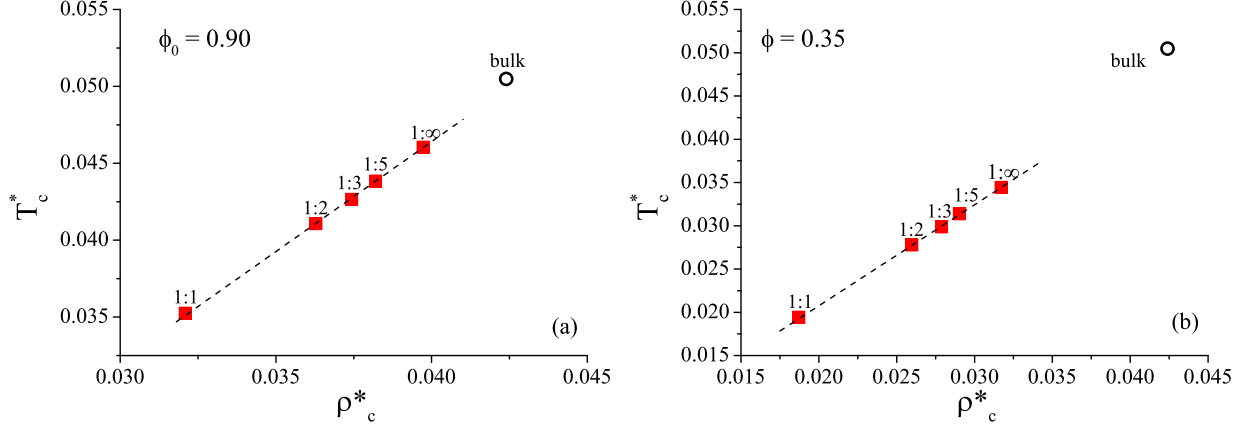


FIG. 7: Critical parameters of the RPM fluid confined in a hard-sphere matrix at different size ratios  $\sigma_1:\sigma_0$  (solid symbols), but at the fixed porosities  $\phi_0 = 0.90$  (a) and  $\phi = 0.35$  (b). Open symbol corresponds to the RPM fluid in the bulk. The results are obtained by using equation (18).

#### IV. CONCLUSIONS

We have studied the effects of disordered porous media on the vapour-liquid phase behaviour of a model ionic fluid consisting of an electroneutral equimolar mixture of equisized charged hard spheres immersed in a structureless dielectric continuum (the so-called RPM model). To this end, based on an extended Madden-Gland model, we have developed a theoretical approach which combines the method of CVs with the SPT theory reformulated recently for a hard-sphere fluid confined in a disordered hard-sphere matrix. While the CV theory appears to be successful in studying the phase behaviour of the systems with Coulomb interactions, the SPT provides an accurate analytical description of the thermodynamic properties of the reference system, i.e., the system including a hard-sphere repulsion. We have formulated a theory for the system in which, in addition to a hard-core repulsion, pair (repulsive/attractive) interactions between the matrix particles and between the ions and the matrix particles are taken into account.

In this contribution, we have obtained an analytical expression for the chemical potential of a model ionic fluid in a disordered matrix formed by uncharged hard spheres in the RPA. Based on this expression, we have calculated the vapor-liquid binodals and have analyzed the effects of the matrix characteristics (geometrical and probe-particle porosities and a size ratio of matrix and fluid particles) on the coexistence envelope. Also, using the method proposed

previously for the bulk RPM, we have derived an explicit equation for the vapour-liquid spinodal which takes into account the effects of the third- and fourth-order correlations. Since this method allows us to obtain a good quantitative agreement with simulation data for the critical parameters of an unconfined RPM, we suppose that it has produced reasonable quantitative results for the system under consideration. Both approximations have yielded the same dependence of the vapour-liquid phase diagram on the matrix characteristics, i.e., with a decrease of porosity the critical point shifts toward lower fluid densities and lower temperatures and the region of coexistence is getting narrower. It has also been observed that for the fixed matrix porosity, both the critical temperature and the critical density increase with an increase of the size of matrix particles and tend to the critical values found for the bulk RPM.

In conclusion, the vapour-liquid behaviour of the RPM confined in random hard-sphere matrices characterized by different porosities and by different hard-sphere diameters has been studied for the first time. The RPM is the simplest model of ionic fluids which does not take into account the charge, size and shape asymmetry of ions being usually typical of real ionic systems. Thus, the theory should be developed to be capable of describing phase diagrams of more complex models. The work in this direction is in progress.

## Appendix

Quantities  $S_3$  and  $S_4$  given by (19) can be presented in terms of the derivatives with respect to  $\eta_1$  ( $\eta_1 = \frac{\pi}{6}\rho_1\sigma_1^3$ ) as follows:

$$S_3 = S_2 \left( S_2 + \eta_1 \frac{\partial S_2}{\partial \eta_1} \right), \quad (\text{A24})$$

$$S_4 = S_2 \left[ S_2^2 + 4S_2\eta_1 \frac{\partial S_2}{\partial \eta_1} + \eta_1^2 \left( \frac{\partial S_2}{\partial \eta_1} \right)^2 + S_2\eta_1^2 \frac{\partial^2 S_2}{\partial \eta_1^2} \right]. \quad (\text{A25})$$

Then, one can find explicit expressions for  $S_2$ ,  $S_3$  and  $S_4$  by using the formulae

$$S_2 = \left[ \frac{1}{1 - \eta_1/\phi_0} + \frac{\eta_1}{\phi(1 - \eta_1/\phi_0)^2} + \frac{A\eta_1}{\phi_0(1 - \eta_1/\phi_0)^3} + \frac{2B\eta_1^2}{\phi_0^2(1 - \eta_1/\phi_0)^4} \right]^{-1}, \quad (\text{A26})$$

$$\frac{\partial S_2}{\partial \eta_1} = -GS_2^2, \quad \frac{\partial^2 S_2}{\partial \eta_1^2} = -FS_2^2 + 2G^2S_2^3, \quad (\text{A27})$$

$$G = \frac{1}{\phi_0(1 - \eta_1/\phi_0)^2} + \frac{1 + \eta_1/\phi_0}{\phi(1 - \eta_1/\phi_0)^3} + \frac{A(1 + 2\eta_1/\phi_0)}{\phi_0(1 - \eta_1/\phi_0)^4} + \frac{4B\eta_1(1 + \eta_1/\phi_0)}{\phi_0^2(1 - \eta_1/\phi_0)^5}, \quad (\text{A28})$$

$$F = \frac{2}{\phi_0^2(1 - \eta_1/\phi_0)^3} + \frac{2(2 + \eta_1/\phi_0)}{\phi\phi_0(1 - \eta_1/\phi_0)^4} + \frac{6A(1 + \eta_1/\phi_0)}{\phi_0^2(1 - \eta_1/\phi_0)^5} + \frac{4B(1 + \eta_1/\phi_0)}{\phi_0^2(1 - \eta_1/\phi_0)^5} + \frac{8B\eta_1(3 + 2\eta_1/\phi_0)}{\phi_0^3(1 - \eta_1/\phi_0)^6} \quad (\text{A29})$$

which are obtained from (20) and (23).

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